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ELECTROLESS PLATING PROCESS

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8 Claims

ABSTRACT OF THE DISCLOSURE

A process for plating non-conductive materials such as plastics by means of an electroless transition metal plating bath at a temperature below the deformation temperature of the non-conductive material to be plated. The process provides for the sensitizing of the material to be plated and thereafter immersing the sensitized material in a plating bath comprising an aqueous solution of a transition metal salt, a transition metal reducing agent, a ligand complexing agent, and a carbonate buffering agent wherein the bath is maintained at a pH in the range of 7 to 11. The material to be plated is left in the bath until plating to the desired depth has been accomplished and the plated material is thereafter removed.

This invention relates to electroless transition metal plating and in particular to a process for plating plastics and other materials in a low temperature plating bath.

Electroless transition metal plating relates to the autocatalytic deposition of a transition metal such as nickel, cobalt and iron on a catalytic surface. Materials which are catalytic to such plating baths include iron, cobalt, nickel, palladium, gold, aluminum and platinum. Other elements which have to be pretreated to render them catalytic include copper and silver. In general the materials used with these baths have been metals which do not deform or lose their shape at the operating temperature of such plating baths.

In various instances, it is desirable to be able to plate a non-catalytic material such as plastic. For example, there are many uses in the automotive industry for metal plated plastics. To this end there has been developed processes utilizing plating baths which are suitable for plating on plastic materials and other non-conductors. Plating baths heretofore developed for such materials have generally required a temperature of at least 150° F. in order to produce plating at a practical rate. Below this temperature these baths are either incapable of plating or plate at such a low rate that their use on a production basis is not feasible. However, because such non-conductive materials are frequently sensitive to heat and will deform if placed in a bath that has a temperature above 150° F., the processes have been limited to use with plastics having a high temperature deformation point.

Specific examples of plastic materials which could not be plated include A.B.S. (acrylonitrile-butadiene-styrene) and polyesters. Such materials cannot endure temperatures in excess of 140° F. without being subject to serious deformation. Because these specific plastics are widely used in such applications as decorative stripping and on radios, heaters, etc. in automobiles, it is desirable that a method be found for plating transition metals, especially nickel on them.

The present invention provides a process which produces plating at a rate comparable to presently known baths. At the same time, the process is operable at a relatively low temperature and hence is suitable for use in the plating of plastics and other non-conductive materials where a low temperature bath is a prime requisite. The process com-

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prises the steps of sensitizing the material to be plated such that it is rendered catalytic to a transition metal plating bath, thereafter immersing the sensitized material in an electroless transition metal plating bath which has been raised to a temperature not in excess of the deformation point of the material, allowing the sensitized material to remain in the bath until plating in the desired thickness has been obtained thereon, and thereafter removing the plated material from the bath.

In its preferred embodiment, the process of this invention utilizes the electroless bath for plating transition metals such as nickel, cobalt and iron which is described in copending application Ser. No. 479,346 filed Aug. 12, 1965, and now abandoned. Utilization of the plating bath described therein is preferred because such a bath will plate at low temperatures. Where the material to be plated does not deform at low temperatures, the process is also suited for use with conventional electroless transition metal plating baths. By utilizing the baths disclosed in the application just referred to and limiting the operation of the bath to a temperature not in excess of 120° F., the bath of that disclosure produces plating on plastics and other low temperature materials at a satisfactory rate. As disclosed in that application, the bath comprises an aqueous solution of a transition metal salt, a ligand complexing agent, a transition metal reducing agent and a carbonate buffering agent wherein the pH of the bath is adjusted by the buffering agent to a value in the range from about 7 to about 11.

The process of this invention will be more readily understood after reference to the following detailed description.

The first step of the process includes sensitization of the material to be plated prior to immersion in the plating bath. Sensitization relates to the step or steps for making a non-conductive, non-catalytic material catalytic to an electroless plating bath. The result of sensitization is to provide a deposit of a catalytic material over the surface of the non-catalytic material to be plated in sufficient quantities to successfully catalyze the plating reaction once the material is introduced into the electroless plating bath.

In detail, the sensitizing step includes the following. The material to be plated is cleaned to insure that soil, fingerprints, and surface contamination due to handling and storage are completely removed. Non-silicated alkaline-type cleaners are especially suitable for the cleaning operation. Where plastic is the material to be treated, a highly chelated cleaner is preferable. Thorough cleaning of the material to be plated is a prerequisite for satisfactory etching.

After cleaning, the part is rinsed thoroughly and subjected to an etching solution. A suitable etching solution comprises a concentrated solution of chromic acid having a specific gravity in the range of from 1.6 to 1.68. Other etching baths such as those described in Metallizing of Plastics, Harold Narcus, Reinhold Publishing Co., 1960, are also suitable.

The cleaned object is placed in the etching solution and allowed to remain for approximately 5 to 10 minutes. The concentration of the etching solution and the length of etching immersion are chosen such that etching is uniform but not severe enough to degrade the material to be plated. Air or mechanical agitation of the etching solution is helpful in preventing stratification of the constituents of the etching solution and insuring uniform etching. The amount of catalytic material that can be adsorbed into the surface is dependent on the quality of the etching. An etching operation according to the preceding steps produces a finely abrasive surface which is readily wetted and suitable for trapping and holding a sufficient amount

of fine particles of palladium or other catalytic element.

When etched, the object is removed and rinsed thoroughly. Proper rinsing is important in order to remove all traces of the etching material from the object surface so as to not contaminate the sensitizing and plating baths. Contamination, particularly of the plating bath, is undesirable because the stability of such plating baths is frequently adversely affected by such a condition.

After rinsing, the etched material is immersed in a first sensitizing bath comprising an acidic solution of stannous chloride. Sensitizing bath stabilizing agents such as resorcinol and other reducing agents mentioned in Metallizing of Plastics, previously referred to, are normally added to the stannous chloride bath. The stabilizing agent aids the bath in preventing the tendency of the stannous chloride to oxidize to stannic chloride. Immersion in this first sensitizing bath produces a dispersion of stannous chloride on the surface of the object.

The part is then removed from the first sensitizing bath, rinsed and immersed in a second sensitizing solution which comprises a dilute acid solution of palladium chloride. Typical formulations for this solution are also described in the publication Metallizing of Plastics previously referred to. When the stannous chloride-coated object is introduced into the second sensitizer solution, the palladium chloride is reduced to elemental palladium and displaces the dispersion of stannous chloride on the surface of the etched material leaving a dispersion of metallic palladium. The object is now sensitized and capable of catalyzing an electroless plating reaction.

Upon rinsing, the material to be plated is ready for immersion in an electroless plating bath. For plating at a temperature below 120° F. a suitable bath comprises an aqueous solution of a transition metal salt, a ligand complexing agent, a transition metal reducing agent, and a carbonate buffering agent. Typical formulations for such a bath are:

BATH NO. 1

Element	Preferred (grams/liter)	Range (grams/liter)
Nickel added as nickel chloride.....	15.0	5-50
Sodium glycolate.....	23.0	0-100
Glycine.....	8.0	5-30
Sodium hypophosphite.....	25.0	5-50
Sodium carbonate.....	30.0	10-60
pH.....	8.2	7-11

BATH NO. 2

Element	Preferred (grams/liter)	Range (grams/liter)
Iron added as ferrous sulfate.....	30.0	5-60
Potassium citrate.....	60.0	10-100
Cyanoacetohydrazide.....	15.0	5-40
Potassium carbonate.....	40	10-60
Dimethylamine borane.....	1.5	0.5-20
pH.....	8.2	7-11

In the above formulation dimethylamine borane is the reducing agent. Where strong transition metal reducing agents such as water soluble boranes are employed, it is possible to simplify the sensitizing steps described above to a one-step operation. Specifically, a sufficient amount of catalyst is deposited on the surface of the object to be plated by the single immersion in a 10% solution of the second sensitizing bath outlined above.

BATH NO. 3

Element	Preferred (grams/liter)	Range (grams/liter)
Cobalt added as cobalt chloride.....	30.0	5-60
Carboxypimelic acid.....	50.0	10-100
Glycine.....	10.0	5-30
Choline carbonate.....	30.0	10-60
Sodium hypophosphite.....	30.0	5-100
pH.....	8.5	7-11

Other suitable electroless plating baths comprise an aqueous solution of a transition metal-organic coordination compound, a ligand complexing agent, a transition

metal reducing agent and a carbonate buffering agent. Examples of such formulations include:

BATH NO. 4

Element	Preferred (grams/liter)	Range (grams/liter)
Nickel added as nickel glycolate.....	3.75	1-30
Glycine.....	5	1-50
Sodium hypophosphite.....	10	1-100
Potassium carbonate.....	20	10-60
pH.....	8.0	7-11

BATH NO. 5

Element	Preferred (grams/liter)	Range (grams/liter)
Nickel added as nickel acetate.....	3.75	1-30
Carboxypimelic acid.....	5	1-50
Sodium hypophosphite.....	10	1-100
Sodium carbonate.....	20	10-60
pH.....	8.0	7-11

Baths having the general formulations outlined above will plate at a temperature of approximately 60° F. To obtain plating on most plastic and other non-conductive materials, it is sufficient to maintain the bath at a temperature not in excess of 120° F. Provided the object to be plated remains sufficiently rigid in baths at temperatures above 120° F. the process of this invention can also be performed with electroless baths whose effective plating temperature is in excess of 120° F.

The sensitized object is left in the bath until plating in the desired thickness has been obtained. When the object has been immersed in the bath for the length of time necessary to produce the desired plating thickness, it is then removed. After rinsing, the object is ready for electroplating or other desired finishing operations preparatory to use as a finished product.

What is claimed is:

1. A process for plating transition metals on non-conductive materials comprising the steps of:

(1) sensitizing the surface of the material to be plated such that it is catalytic to an electroless transition metal plating bath,

(2) immersing the sensitized material to be plated in an electroless transition metal plating bath comprising an aqueous solution of a transition metal organic compound, a ligand complexing agent, a transition metal reducing agent and a carbonate buffering agent wherein the pH of the bath is maintained at a value in the range from about 7 to 11,

(3) maintaining the bath at a temperature below the deformation temperature of the material to be plated,

(4) allowing the material to be plated to remain in bath until plating in the desired thickness has been achieved, and

(5) removing the plated material from the bath.

2. A process for plating transition metals on non-conductive materials comprising the steps of:

(1) sensitizing the surface of the material to be plated such that it is catalytic to an electroless transition metal plating bath,

(2) immersing the sensitized material to be plated in an electroless transition metal plating bath comprising an aqueous solution of a transition metal organic coordination compound, a ligand complexing agent, a transition metal reducing agent, and a carbonate buffering agent wherein the pH of the bath is maintained at a value in the range of from about 7 to about 11,

(3) maintaining the bath at a temperature below 120° F.,

(4) allowing the material to be plated to remain in the bath until plating in the desired thickness has been achieved, and

(5) removing the plated material from the bath.

3. A process for plating transition metals on non-conductive materials comprising the steps of:

(1) etching the surface of the material to be plated,

- (2) sensitizing the etched surface such that it is catalytic to an electroless transition metal plating bath,
- (3) immersing the sensitized material to be plated in an electroless transition metal plating bath comprising an aqueous solution of a nickel-organic compound, a ligand complexing agent for diminishing competition from ions other than reducing and complexing anions for coordination positions of the nickel, a nickel reducing agent, and a carbonate buffering agent wherein the pH of the bath is maintained within the range of from about 7 to 11,
- (4) maintaining the bath at a temperature below 120° F.,
- (5) allowing the material to be plated to remain in the bath until plating in the desired thickness has been achieved, and
- (6) removing the plated material from the bath.

4. A process for plating transition metals on non-conductive materials comprising the steps of:

- (1) etching the surface of the material to be plated,
- (2) depositing a dispersion of a catalytic material on the etched surface,
- (3) immersing the material to be plated in an electroless transition metal plating bath comprising an aqueous solution of a nickel-organic coordination compound, a ligand complexing agent selected from the class consisting of glycine, citric acid, carboxypimelic acid, cyanoacetic acid, glycolic acid, propionic acid, formic acid, and salts thereof, a hypophosphite reducing agent, and a carbonate buffering agent wherein the pH of the bath is maintained within the range of from about 7 to about 11,
- (4) maintaining the bath at a temperature below 120° F.,
- (5) allowing the material to be plated to remain in the bath until plating in the desired thickness has been achieved, and
- (6) removing the plated material from the bath.

5. A process according to claim 4 wherein the step of depositing a dispersion of a catalytic material on the etched surface comprises the steps of:

- (1) immersing the etched material in a first sensitizing bath, and thereafter
- (2) immersing the material in a second sensitizing bath.

6. A process according to claim 5 wherein the step of etching the surface of the material to be plated comprises placing the material in a chromic acid solution having a specific gravity in the range of 1.6 to 1.68, wherein the step of immersing the etched material in a first sensitizing bath comprises immersing the material in a stannous chloride solution to produce a pre-sensitizing stannous chloride deposit on the etched surface, and wherein the step of immersing the material in a second sensitizing bath comprises immersing the pre-sensitized material in a palladium chloride solution to produce a dispersion of metallic palladium on the etched surface.

7. A process for plating nickel on non-conductive materials comprising the steps of:

- (1) etching the surface of the material to be plated,
 - (2) immersing the etched material in a sensitized bath,
 - (3) preparing a nickel plating bath by preparing an aqueous solution of nickel glycolate in the range of 1 to 30 grams/liter to which is added glycine in the range of 1 to 50 grams/liter, a nickel reducing agent in the range of 1 to 100 grams/liter, and a carbonate buffering agent in the range of 10 to 60 grams/liter wherein the pH of the bath is maintained within the range of from about 7 to about 11,
 - (4) immersing the sensitized material to be plated in the plating bath,
 - (5) maintaining the plating bath at a temperature below 120° F.,
 - (6) allowing the material to be plated to remain in the bath until plating in the desired thickness has been achieved, and
 - (7) removing the plated material from the bath.
8. A process for plating nickel on non-conductive materials comprising the steps of:
- (1) etching the surface of the material to be plated,
 - (2) immersing the etched material in a first sensitizing bath,
 - (3) preparing a nickel plating bath by preparing an aqueous solution of nickel acetate in the range of 1 to 30 grams/liter to which is added carboxypimelic acid in the range of 1 to 50 grams/liter, a nickel reducing agent in the range of 1 to 100 grams/liter, and a carbonate buffering agent in the range of 10 to 60 grams/liter wherein the pH of the bath is maintained within a range of from about 7 to about 11,
 - (4) immersing the sensitizing material to be plated in the nickel plating bath,
 - (5) maintaining the nickel plating bath at a temperature below 120° F.,
 - (6) allowing the material to be plated to remain in the bath until nickel plating in the desired thickness has been achieved, and
 - (7) removing the plated material from the bath.

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